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A fully bio-based polyimine vitrimer derived from fructose†

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A bio-based polyimine vitrimer containing 100% renewable carbon content has been synthesised and characterised. This vitrimer material was prepared by combining a bio-based furan dialdehyde obtained from fructose with a bio-based diamine and triamine prepared from fatty acids. Due to the dynamic nature of the imine reversible bonds, the vitrimer properties can be clearly demonstrated. The obtained films exhibit fast stress relaxation around room temperature. To the best of our knowledge, this is the first report of a fully bio-based polyimine vitrimer.

Global plastic pollution has urged the scientific community to create new solutions to increase the intrinsic controlled degradability of polymers, and one promising strategy is the implementation of dynamicity in these materials. Dynamicity is imparted to materials in the presence of labile noncovalent and dynamic covalent bonds capable of undergoing reversible formation and cleavage thereby endowing the corresponding materials with innovative properties.^{1,2}

Dynamic polymers have emerged over the last couple of decades, first with the introduction of supramolecular polymers in 1990 by Lehn and co-workers,^{3,4} followed by the introduction of dynamic covalent polymers in 2002 by Wudl and co-workers⁵ as well as the development of DYNAMERs by Lehn and co-workers.^{6–8} The term Covalent Adaptive Networks (CANs) was consequently coined by Bowman and co-workers to design specifically cross-linked polymer networks exhibiting reversible bonds.⁹ CANs are classified into two different types of exchange mechanisms: dissociative and associative.¹⁰ Upon heating, dissociative CANs depolymerize and show a decrease

in connectivity, whereas associative CANs do not depolymerize and retain a fixed cross-link density.

The concepts of DYNAMERs and CANs were further enriched and developed for thermosets by Leibler and co-workers in 2011,¹¹ showing that the covalent bonds in the thermosets can be rendered reversible in the presence of a catalyst. They coined the term vitrimer for these materials: vitrimers are cross-linked polymer networks (associative CANs) made of covalently bound chains forming an organic network that exhibits silica-like behavior, *i.e.* a gradual decrease of viscosity upon heating, endowing them with unique properties compared to classical thermosets, such as self-healing, reprocessability and network rearrangement without the loss of integrity.¹⁰ These properties allow direct recyclability of vitrimers and as such are excellent candidates for renewable polymeric materials.¹² On the other hand, bio-based polymers hold great promise for the development of sustainable materials; the integration of vitrimer properties within bio-based materials therefore appears as an innovative and pioneering combination.

To date, only a few examples of bio-based vitrimers have been reported in the literature.^{13–19} One recent example uses ozone treated Kraft lignin (mainly in 1,4-dioxane) cured with sebacic acid epoxy combined with a zinc catalyst to form vitrimers *via* transesterification exchange reactions.¹⁶ Another example of bio-based vitrimers combines a lignin-based monomer vanillin with diamines to form Schiff base vitrimers (in trichloromethane).¹⁶ A fully bio-based system was prepared by Altuna and co-workers, forming networks from epoxidized soybean oil and citric acid in the presence of water without a catalyst (although full stress relaxation could not be achieved in this system).²⁰ However, these examples do not present vitrimers containing 100% renewable carbon. Here we report, to the best of our knowledge, the first fully bio-based vitrimer containing 100% renewable carbon made of a polyimine network. The cross-linked polyimine is prepared from the bio-based monomer 2,5-furandicarboxaldehyde (FDC) and a dimeric and trimeric amine bio-based mixture DTA (0.75 : 0.25

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ratio, respectively,²¹ commercialised as Priamine 1071 by Croda).

DTA is used as a building block in epoxy resins for indoor and outdoor coating applications and can be produced from biobased feedstocks, and more particularly from vegetable oils.²¹ Being both bio-based and commercially available, **DTA** already presents a viable economic solution to an available bio-based mixture of a diamine and triamine. Monomer **FDC** is obtained from a bio-based fructose *via* 5-(hydroxymethyl)furfural (**HMF**) with a synthesis based on several principles of green chemistry (Fig. 1). Green synthesis of **FDC** from fructose has been an active research area in recent years,^{22–25} in particular studies describing a one-pot synthesis using recyclable catalysts.^{22,25} Direct green synthesis of **FDC** from **HMF** is also a blooming research topic in green chemistry.^{26–31} The interest in the difunctionalized furan derived from **HMF** is demonstrated by the recent opening of a 60-metric-ton-per-year furandicarboxylic methyl ester (**FDME**) pilot plant by DuPont and ADM in order to produce polytrimethylene furandicarboxylate (**PTF**), a fully bio-based plastic that can be used for beverage bottles and other applications now served by polyethylene terephthalate (**PET**).³²

Imines have already been used as reversible linkages in dynamic materials,^{33–40} albeit only a handful of polyimine vitrimers have been reported.^{18,41} Imine bonds have been chosen as dynamic bonds in this study due to both the bio-based availability of the monomers and the extensive knowledge on imine dynamicity.^{42–44} Fast exchange of imines, compared to most reversible bonds employed in vitrimers, also show promising results to lower both the synthesis and reprocessability temperatures.^{1,42} Three different mechanisms of imine exchange have been reported: (i) imine hydrolysis, (ii) amine exchange and (iii) imine metathesis.⁴⁵ It has been demonstrated that an excess of amines will drive the exchange of imines *via* a transimination mechanism, with the formation

of amination intermediates.⁴⁵ Du Prez and co-workers have recently shown that an excess of amines gives faster stress relaxation times in vinylogous urethane vitrimers.⁴⁶ Consequently, in order to trigger an associative exchange mechanism, which is essential to maintain the integrity of the network, we chose to use an excess of amines. **FDC** and **DTA** were mixed in a 1 : 1.2 molar ratio in THF in the absence of a catalyst (Fig. 2). After some preliminary tests, THF was selected as a solvent due to the structural similarities with **FDC**, making it a solvent of choice in this particular reaction, as well as the fact that THF has been shown to be potentially bio-based.⁴⁷ The reaction was left to stir at room temperature for an hour. The solvent was removed by solvent casting overnight before curing for another hour at 120 °C in a hot press, yielding vitrimer **1** as a dark red opaque elastomeric film (Fig. S1, ESI†).

The polymerization was confirmed by FTIR measurements with the disappearance of the vibration band characteristics of the aldehyde bond at 1663 cm^{−1} and the appearance of the vibration band of the imine bond at 1639 cm^{−1} (Fig. S2, ESI†). The thermostability of vitrimer **1** was then analysed by TGA under an air atmosphere. Using a heating rate of 10 K min^{−1}, the degradation onset starting at 5% weight loss was observed around 300 °C, showing robustness towards reprocessability (Fig. S3, ESI†). Isothermal analysis at 120 °C for 2 h evidenced the stability of the material under the above-stated synthesis conditions (Fig. S4, ESI†). The DSC thermogram revealed a glass transition temperature (*T*_g) around −10 °C (Fig. S5, ESI†). The viscoelastic properties of vitrimer **1** were then studied using stress relaxation and creep recovery experiments. For stress relaxation experiments, a constant strain of 2%, in the viscoelastic region, was applied and the relaxation modulus was followed as a function of time between 40 °C and 80 °C (Fig. 3, left). Full stress relaxation was achieved as a function of time, ranging from 40 s at 80 °C to 1300 s at 40 °C. Full stress

Fig. 1 General scheme of 2,5-furandicarboxaldehyde (**FDC**) synthesis from fructose *via* 5-(hydroxymethyl)furfural (**HMF**).

Fig. 2 Synthesis of polyimine vitrimer **1** from **FDC** and **DTA**.

Fig. 3 Stress relaxation plots of vitrimer 1 between 40 °C and 80 °C: (left) stress relaxation curves and (right) Arrhenius plots obtained from the stress relaxation values at $G/G_0 = 1/e$.

relaxation was also recorded at room temperature, yielding a complete stress relaxation in less than an hour. This result is due to the reversibility of the imine bonds in the polyimine network, facilitated by an excess of amines. The system relaxation follows a Maxwell model, and can be fitted to the Arrhenius law using relaxation times at $t^* = 1/e$ (Fig. 3, right). The relationship between $\ln(t^*)$ and $1000/T$ is subsequently used to extract the activation energy from the Arrhenius equation using the slope of the equation (see the ESI† for calculation details). The activation energy obtained from stress relaxation for vitrimer 1 is 64 kJ mol^{-1} . This is in good agreement with similar systems in the literature such as the vanillin-based polyimine vitrimers developed by Zhu and co-workers, which reported an activation energy value ranging from 49 to 81 kJ mol^{-1} depending on the diamine used in the synthesis.¹⁸ Several studies have been published by Zhang and co-workers on vitrimer-like polyimines, using a combination of dialdehydes, diamines and triamines.^{33–37} They have obtained, using stress relaxation experiments, an activation energy of 157 kJ mol^{-1} . This higher value, compared to our system, could be explained by the use of shorter carbon chains giving an increased rigidity to the system. More recently, a polyimine vitrimer system, very similar to the one developed by Zhang and co-workers, has been reported in which the main difference is that the aliphatic diamines have been replaced by aro-

matic diamines.⁴¹ This change leads to a lower energy activation of 80 kJ mol^{-1} . One of the hypotheses to explain the fast relaxation observed in our system is the length of the amine carbon chains, which is longer than that of the previously reported polyimine vitrimers.

To correlate the results from stress relaxation experiments, creep recovery experiments were carried out. A constant stress of 2000 Pa was applied over 1000 s followed by a recovery time of 1000 s, recorded for temperatures between -10 °C and 40 °C (Fig. 4, left). Above 0 °C , a permanent deformation of the elastomeric vitrimer 1 can be seen. This phenomenon is due to the fast dynamic transimination exchange taking place inside the vitrimer material, leading to permanent deformation up to 7% at 40 °C . This effect further demonstrates the rapidity of the imine exchange within vitrimer 1. The rate of deformation, also called the creep rate (ϵ'), has been shown by Du Prez and co-workers to also be an efficient method to calculate the activation energy of the system.⁴⁶ The relationship between $\ln(\epsilon')$ and $1000/T$ can be fitted to the Arrhenius law (Fig. 4, right) and the energy activation is extracted from the slope of the equation (see the ESI† for calculation details). The activation energy obtained from stress relaxation is found to be 60 kJ mol^{-1} , which is in very good agreement with the value obtained from stress relaxation experiments.

Fig. 4 Creep experiment plots of vitrimer 1: (left) creep recovery with an applied stress of 2000 Pa for 1000 s and a recovery time of 1000 s between -10 °C and 40 °C and (right) Arrhenius plots extracted from creep recovery experiments between 10 °C and 50 °C .

A topology freezing transition temperature characteristic of vitrimers, coined T_v , was introduced by Leibler and co-workers in 2011. This characteristic temperature is defined as the temperature above which a solid to liquid transition occurs with a viscosity of $\eta = 10^{12}$, *i.e.*, the temperature above which the network topology can be rearranged by dynamic exchange.¹¹ The Maxwell equation is usually employed to extract T_v from the relaxation time using the Arrhenius equation obtained from stress relaxation experiments (see the ESI† for calculation details). A theoretical T_v of around -60°C was thus obtained for vitrimer 1, using DMA frequency sweep measurements (Fig. S6 and calculations in the ESI†). The obtained T_v , albeit low, is in agreement with the reported vitrimer system.⁴⁸ The behavior of the system is therefore governed by T_g .¹⁰

Swelling experiments were performed on vitrimer 1 to assess the material's resistance to chemical solvents and to ensure the robustness of the cross-linked network. These experiments were performed by immersion of samples for two days at 25°C , in tetrahydrofuran (THF), ethanol (EtOH) and dimethylformamide (DMF). The solubility fraction and swelling ratios obtained are reported in Table 1. As expected, THF is the solvent in which vitrimer 1 shows the highest solubility and swelling ratio (Table 1 and Fig. S7, ESI†). Nevertheless, after several months in THF, the sample remained undissolved. On the other hand, in both DMF and EtOH, the samples show significant swelling, with almost no solubility of the network after 2 days (Table 1 and Fig. S8, ESI†). An interesting experiment to qualitatively probe the dynamicity of the polyimine vitrimer network is to submerge the material in the presence of an excess of a primary amine. In this case, butylamine was selected and added in excess to vitrimer 1, in THF at room temperature (Fig. S7, ESI†). This experiment resulted in a complete dissolution of vitrimer 1 overnight, caused by dynamic amine exchanges that lead to a total depolymerisation of the network.

In the prospect of potential applications for these vitrimer compounds, the hydrolytic stability of vitrimer 1 was tested in neutral, acidic and basic water (Fig. S8, ESI†). After 48 h at 25°C under these versatile conditions, no significant change was observed. Both the soluble fraction and the swelling ratio remained very small (Table 1). The extreme stability of vitrimer 1 under these hydrolytic conditions can be partially attributed to the hydrophobic nature of the amines used. It is important to note that imine bonds are susceptible to hydrolysis, there-

Table 1 Soluble fraction and swelling ratio of vitrimer 1 after 48 h immersion in solvent at 25°C

Solvent	Soluble fraction (%)	Swelling ratio (%)
THF	39.0	237
EtOH	0.7	26
DMF	0.6	14
Neutral H_2O	0.6	3
1 M NaOH	0.4	1
1 M HCl	0.4	4

Fig. 5 Stress-strain curves of vitrimer 1 for different recycling cycles at room temperature.

Table 2 Mechanical properties of vitrimer 1 after 0 to 3 recycling cycles

Recycling step	Elongation at break (%)	Young's modulus (MPa)	Stress (MPa)
0	24 ± 1	4.4 ± 0.4	0.69 ± 0.03
1	22 ± 2	4.4 ± 0.5	0.71 ± 0.03
2	21 ± 3	5.1 ± 0.5	0.73 ± 0.10
3	23 ± 3	4.9 ± 0.4	0.70 ± 0.07

fore the stability of this material is highly relevant and could be an interesting feature to exploit for future applications.

The mechanical properties of vitrimer 1 were then investigated using uniaxial tensile tests. Reprocessability was also assessed using the same tests, after recycling the material *via* compression molding for 10 minutes at 120°C , which is similar to polyimine vitrimers reported in the literature (for the vanillin-based polyimine vitrimer:¹⁸ 2–10 minutes at 180°C). Samples were reprocessed three times and stress-strain curves were successively drawn (Fig. 5). Elongation at break, Young's modulus and stress at break are given in Table 2. The properties of vitrimer 1 are clearly consistent throughout the successive recycling steps, with an elongation at break ranging from 24 to 21%, a Young's modulus from 4.4 to 5.1 MPa, and a stress at break ranging from 0.69 to 0.73 MPa. These values are consistent with the previously reported vitrimer data,^{35,46,49} with a lower elongation at break and a higher Young's modulus, which can be attributed to the high cross-linking density (25%) and is significant for an elastomeric behavior without a yield point. Consistently, IR, DSC and TGA showed no noticeable degradation after the successive recycling cycles, showing the stability of vitrimer 1 towards reprocessability.

Conclusions

In this work, the first fully bio-based polyimine vitrimer 1 containing 100% renewable carbon was synthesised and character-

ised. This polyimine material was prepared by combining a bio-based furan dialdehyde with a mixture of bio-based amines, using imine bonds as covalent dynamic linkages. The vitrimer properties of the polyimine network were demonstrated around room temperature using stress relaxation and creep recovery, with both experiments giving E_a values in very good agreement. Fast stress-relaxation was obtained close to room temperature, which was attributed to the reversibility of the covalent imine bonds enhanced by the excess of amines used. Furthermore, the reprocessability of this material was shown to proceed without any significant loss of mechanical properties. This work also highlights the potential of imines towards environmentally-friendly vitrimers, due to the low temperatures needed for synthesis and reprocessability compared to most vitrimer systems present in the literature. The stability of vitrimer **1** in different aqueous environments, ranging from basic to acidic, further proved the potential of this material for future applications. Work is now underway towards expanding this family of compounds, in order to enhance some physical properties as well as optimize and exploit the versatile exchange pathways. Preliminary studies have also been undertaken to switch the solvent system to an even greener alternative.

Conflicts of interest

There are no conflicts to declare.

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